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U.S. DEPARTMENT OF ENERGY

First-principles Modeling and Design of Solid-State Interfaces for the Protection and Use of Lithium Metal Anodes

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Project ID: bat373

Overview

Timeline

- Start date: April 1, 2017
- End date: February 28, 2020
- Percent complete: 40%

Barriers

- Barriers addressed
  - Electrochemical Energy Storage
    - ❖ Performance → Beyond Li-ion
    - ❖ Life → Cycling performance
    - ❖ Abuse tolerance → Dendrite prevention

Budget

- Total Funding:
  - DOE share: $890K
  - Contractor share: $99K
- Funding for FY 18:
  - DOE share: $297K
  - Contractor share: $33K

Partners

- None at this time

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Relevance - Objectives

❑ Overall objectives

❖ High-throughput framework to screen materials

- Identify promising solid electrolytes
  - Study interfacial stability of Li-metal/solid electrolytes

❖ Study dendrite-resistant electrolyte

- Understand the underlying science controlling the propagation of dendrites in ionic conductors
- Develop a model and criteria to identify promising solid electrolyte materials that can prevent dendrite propagation.

❑ Objectives this period

- ❖ Screen material stability for potential material
- ❖ Electro-Chemo-Mechanical theory to model dendrite formation and growth in all solid state battery

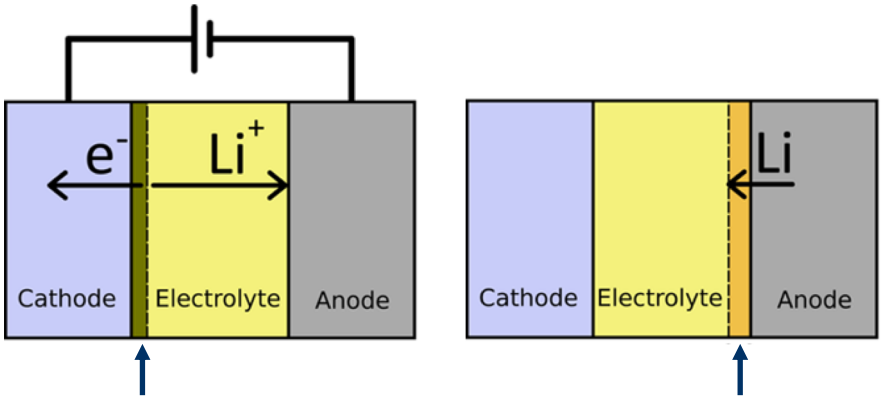
Relevance - Impact

- Improve lack of understanding of Li deposition and interface dynamics in advanced batteries.
- Li metal anodes with solid electrolytes greatly increases energy density and safety of current batteries.
- Improve understanding of complex evolution of Li-metal / solid electrolyte interfaces during electrochemical cycling
- Determine design principles to develop reliable all solid-state batteries

Milestones

Milestone	Month/Year	Status
❖ Stability screening of electrolyte materials using phase diagram assessment of chemical and electrochemical stability	September 2017	Completed
❖ Development of metal-electrolyte electrochemical-mechanical interface model	January 2018	Completed
❖ Determine critical stress conditions that yield fracture in ceramic electrolytes during Li deposition	March 2018	Completed
❖ Evaluation of bulk elastic properties for candidate materials using first principles and atomistic calculations.	June 2018	Ongoing
❖ Li conductivity screening using ab initio molecular dynamics and nudged elastic band method to screen for materials with high Li-mobility.	September 2018	Ongoing

Approach 1 - First Principle Calculation on Chemical Stability and Ionic Conductivity



Li deficient layer

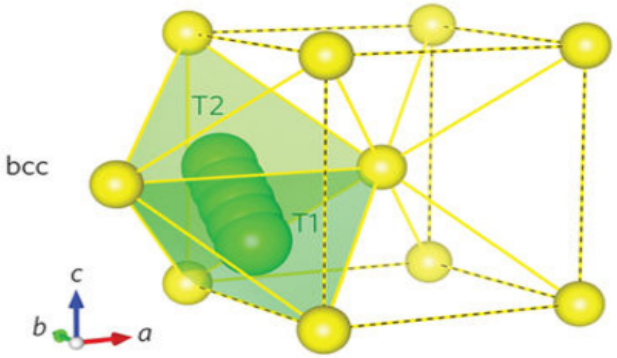
Li rich layer

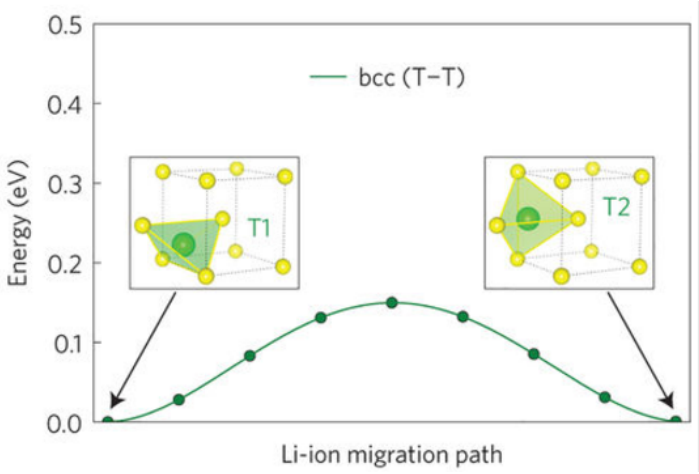
Oxidation limit

Reduction limit

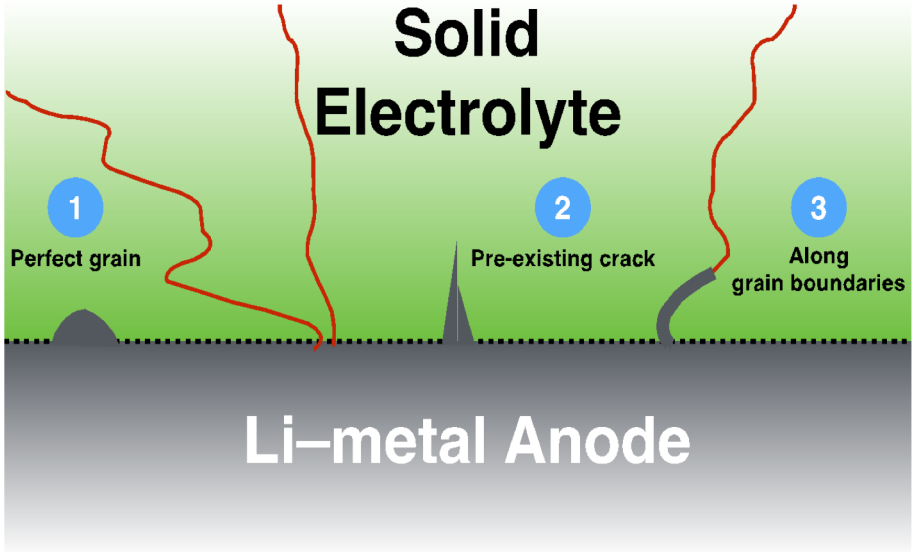
$$\Phi[c, \mu_{\mathrm{Li}}] = E[c] - n_{\mathrm{Li}}[c]\mu_{\mathrm{Li}}$$

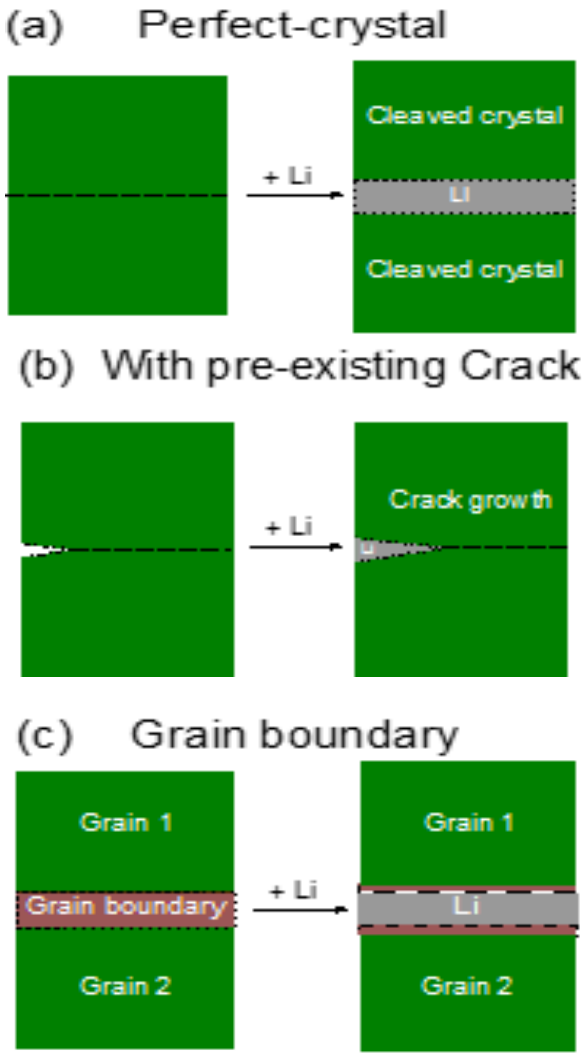
- DFT calculations with PBE GGA using PAW method.
- Nudged Elastic Band (NEB) calculations for energy barriers for single-vacancy migration.
- Defect charge is compensated by a uniform background charge.





Approach 2 – Continuum Theory on Dendrite Formation and Propagation in SSB



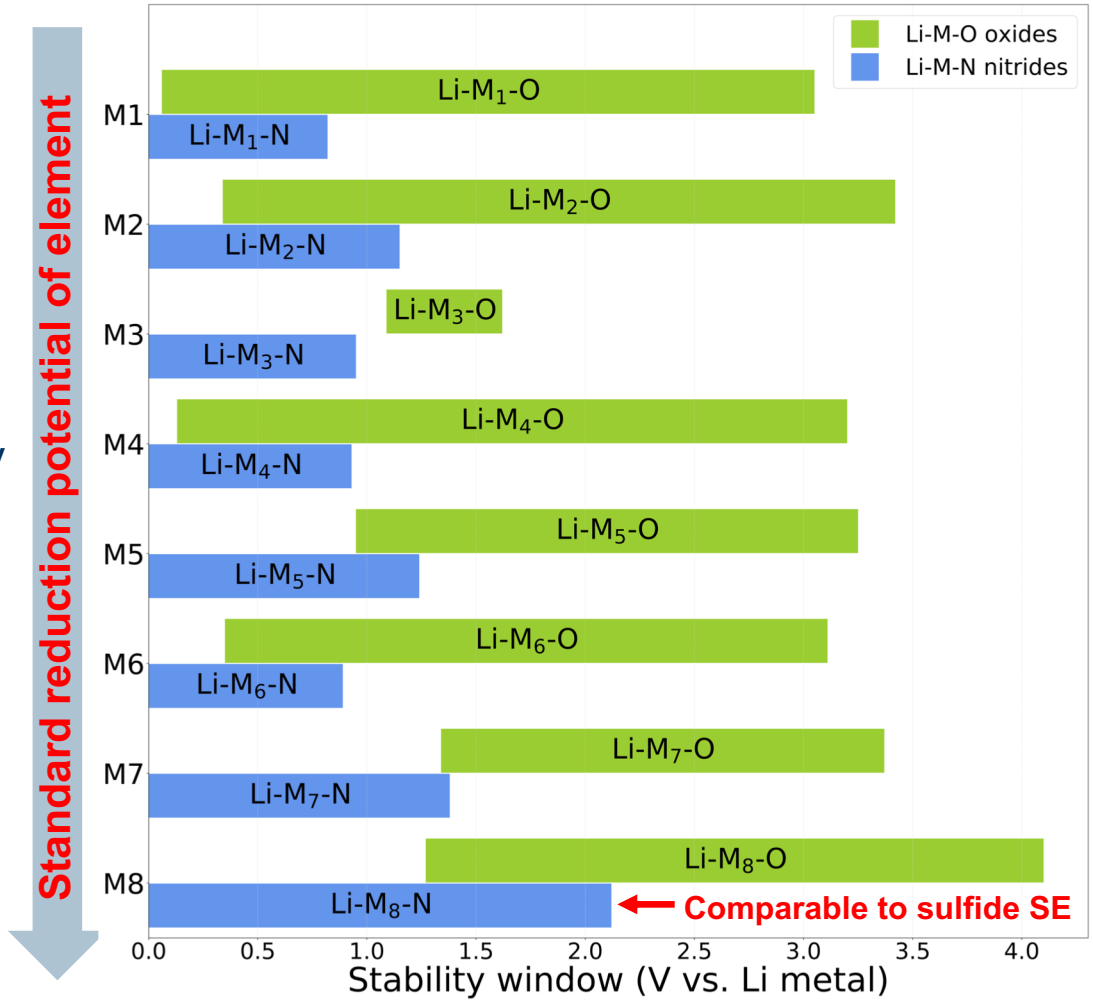


- Mechanism of dendrite nucleation (Model a).
- Mechanism of dendrite growth and crack propagation (Model b).
- Mechanism of dendrite propagation along grain boundary (Model c).

Accomplishments 1 - Electrochemical stability against Li metal

❑ Oxide vs. Nitrides

- ❖ High-throughput calculation of voltage stability window of materials in ICSD database.
- ❖ For the same element M in Li-M-X (X=O or N) ternaries, nitrides exhibit better stability against Li-metal than their oxide counterparts.
- ❖ This result indicates that more covalent M-N bonding can stabilize M from being reduced by Li metal.



Note: exact metal compositions cannot be disclosed at this time

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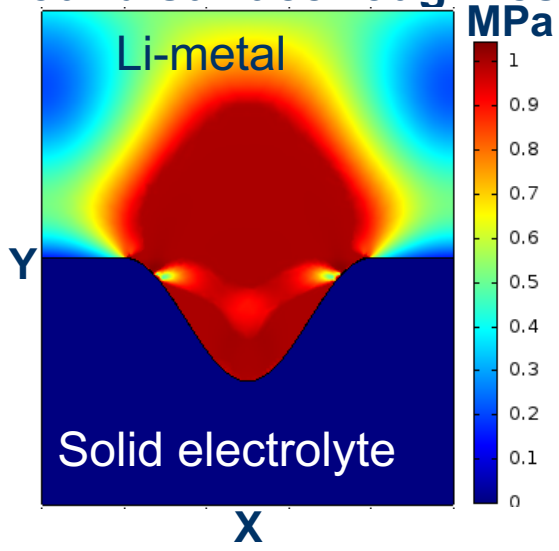
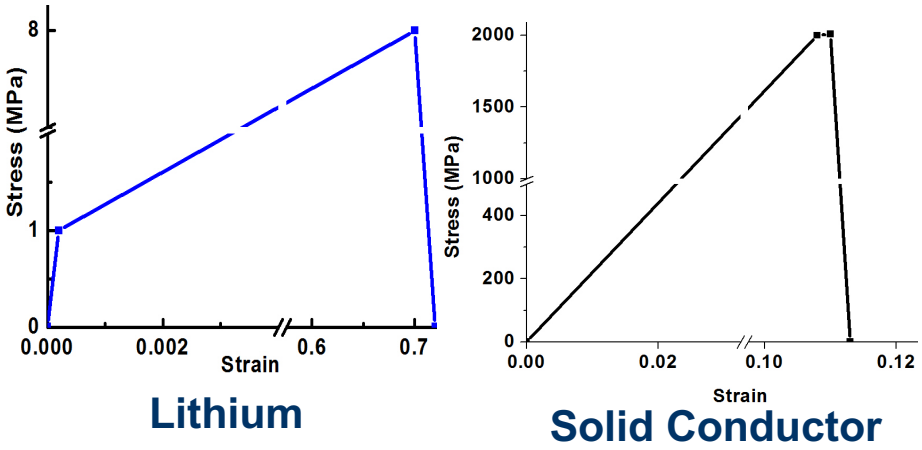
Accomplishments 2 – Stress Distribution and Plasticity of Li metal

❑ **Effective Stress Distribution around surface roughness**

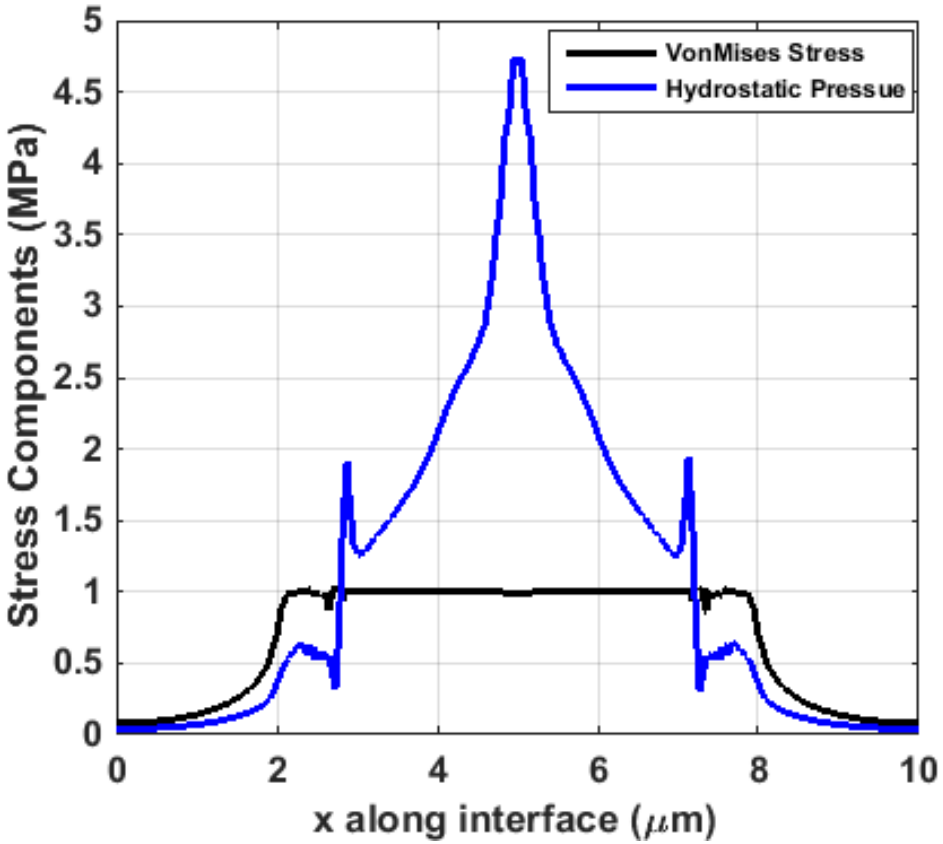


❑ **Stress-Strain Curve**



Lithium **Solid Conductor**

❑ **Stress along interface**



❖ Stress concentrates at the tip of rough surface, which may lead to crack of a solid conductor or protective coating on lithium

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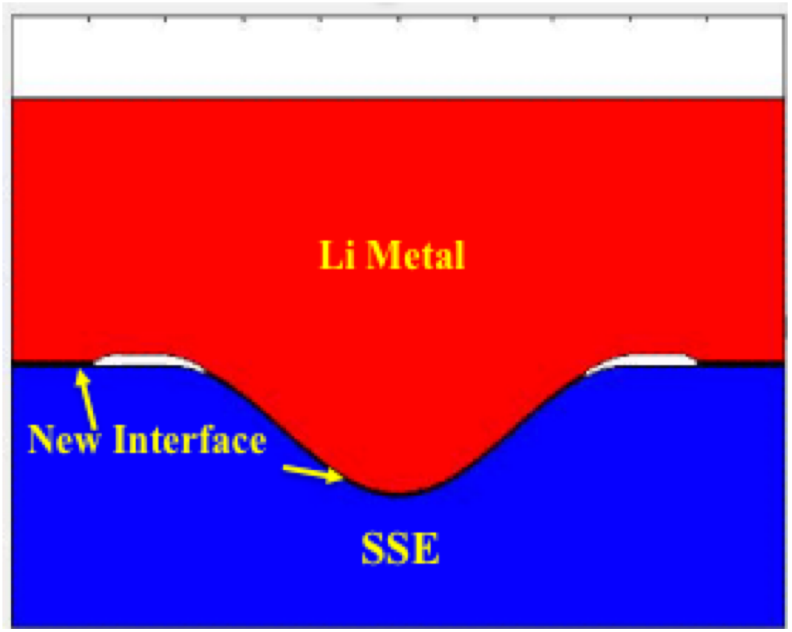
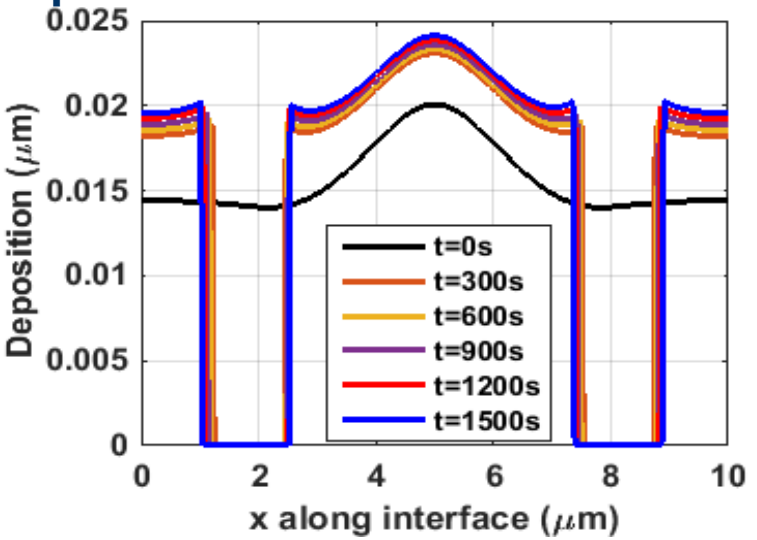
Accomplishments 3 – Inhomogeneous Deposition of Li at Interface

❑ Li Deposition

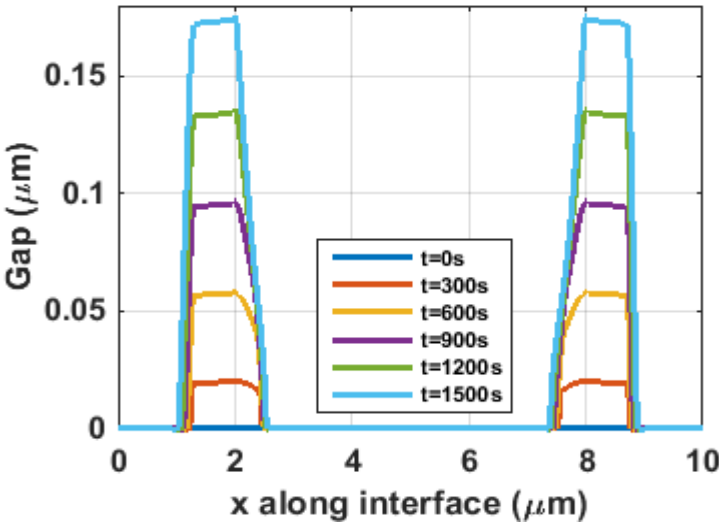


❖ Inhomogeneous deposition on rough surface of solid electrolyte leads to contact loss and dendrite formation.

❖ Deposition at Anode Surface



❖ Gap at Interface



Conclusions

Candidate Solid Electrolytes

- Screened solid electrolytes through large-scale material recognition based on ICSD and materials prediction.
- Used phase diagrams to assess chemical and electrochemical stable solid electrolytes.

Dendrite Formation and Propagation

- Developed a framework to study the stability of interface of solid electrolyte and Li Metal based on first principle calculations.
- Developed continuum method to predict dendrite formation and propagation based on multi-physical coupling method and fracture method.

Responses to Reviewers' Comments

- No previous year comments for this project.

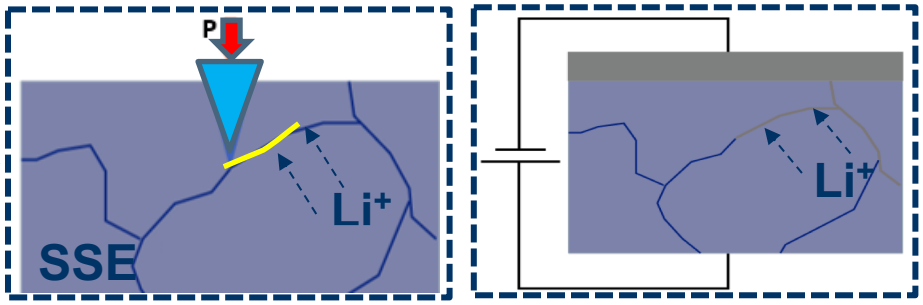
Partners and Collaborations

Most Calculations are done using the following national computing resource:

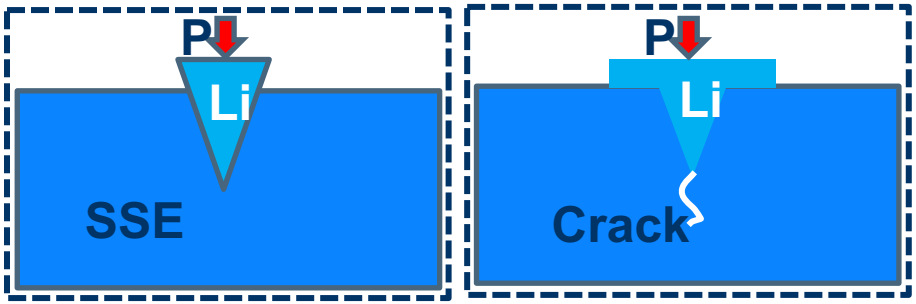
- National Energy Research Scientific Computing Center (NERSC) based at the Lawrence Berkeley National Laboratory;
- Extreme Science and Engineering Discovery Environment (XSEDE);
- Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory and Argonne National Laboratory

Remaining Challenges and Barriers

- **Grain boundary in solid conductor**
  - Diffusion in porous SSE under external pressure
  - Segregation in grain boundary under chemical reaction



- **Fracture Caused by High External Pressure**
  - Losing contact area at interface leads to crack in SSE
  - Incorporate fracture mechanics to describe the propagation of crack and dendrite



Proposed Future Research

- **Task 1: Conductivity Screening**
  - Screening more SE with good ionic conductivity
- **Task 2: Evaluation of bulk elastic properties**
  - DFT calculations of elastic properties for candidate materials
- **Task 3: Critical criteria controlling dendrite propagation**
  - Study the diffusion of Li Metal in Grain boundary and porous material
  - Embedding proper fracture model into the Multiphysics model

Summary

Relevance

- Interfacial stability of Li-metal/solid electrolytes.
- Improve lack of understanding of Li deposition and interface dynamics in advanced batteries.
- Design principles to develop reliable all solid-state batteries

Approach

- First Principle Calculation on Chemical Stability
- Nudged Elastic Band (NEB) used for energy barriers calculation
- Continuum Theory on Dendrite Formation and Propagation in SSB

Technical accomplishments

- More covalent M-N (M = O or N) bonding could stabilize M from being reduced by Li metal.
- Li metal oxides react with Li to form electron conductive phase, making the interface decomposition non-passivating
- Stress will concentrate at the tip of rough surface, leading to cracking solid conductor.
- Inhomogeneous deposition lead to contact loss and dendrite formation in solid state battery

Proposed future research

- Properties of grain boundary in solid conductor
- Fracture Caused by High External Pressure